

Pressure-Temperature Phase Diagram of Multiferroic $Ni_3V_2O_8$

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(Dated: February 6, 2008)

The pressure-temperature phase diagram of multiferroic $Ni_3V_2O_8$ is investigated for hydrostatic pressures up to 2 GPa. The stability range of the ferroelectric phase associated with the incommensurate helical spin order is reduced by pressure and ferroelectricity is completely suppressed at the critical pressure of 1.64 GPa at 6.2 K. Thermal expansion measurements at ambient pressure show strong step-like anomalies of the lattice parameters associated with the lock-in transition into the commensurate paraelectric phase. The expansion anomalies are highly anisotropic, the related volume change is consistent with the high-pressure phase diagram.

PACS numbers: 75.30.-m, 75.30.Kz, 75.50.Ee, 77.80.-e, 77.84.Bw

The Kagomé staircase compound $Ni_3V_2O_8$ is one of the multiferroic magnetoelectric compounds that has recently attracted attention because of the complex phase sequence of several magnetic transitions upon decreasing temperature and the appearance of ferroelectricity in one of the magnetic phases.^{1,2} The origin of ferroelectricity in a limited temperature range ($3.9 \text{ K} < T < 6.5 \text{ K}$) has been a matter of discussion and it was associated with a particular type of magnetic order of the nickel spins. The nickel ions in this compound form a quasi-planar buckled Kagomé staircase in which magnetic frustration is immanent due to the geometry and the antiferromagnetic (AFM) exchange interactions. Due to the buckling of the Kagomé plane there are inequivalent nickel sites and the magnetic exchange interactions between the different nickel spins include first and second nearest-neighbor isotropic Heisenberg interactions as well as magnetic anisotropy and the antisymmetric Dzyaloshinskii-Moriya interactions.² This multitude of magnetic interactions and the geometrical frustration in the Kagomé structure give rise to a cascade of magnetic phase transitions upon decreasing temperature. The magnetic structure of $Ni_3V_2O_8$ has been completely resolved by neutron scattering experiments only recently.^{1,3} The high-temperature paramagnetic phase is orthorhombic, space group $Cmca$ (No 64). With decreasing temperature, magnetic order sets in at $T_N=9.8 \text{ K}$ into an incommensurate (IC) sinusoidal (collinear) spin structure (HTI phase, we follow the notations of Lawes et al.¹). At $T_{C1}=6.5 \text{ K}$ the spin structure changes to a helical spin density wave breaking the spatial inversion symmetry with the onset of ferroelectricity (LTI phase). Upon further cooling, at $T_{C2}=3.9 \text{ K}$, a phase transition into a commensurate magnetic structure takes place (C phase). The C phase is paraelectric and the magnetic order in this phase is symmetric with respect to the spatial inversion operation. The magnetic symmetries in the HTI, LTI, and C phases have been discussed in great detail in recent publications.^{3,4,5} Another transition into a second commensurate magnetic phase at $T_{CC'}$ (C' phase) concludes the sequence of transitions. The magnetic phase diagram

has been explored extensively.^{1,2,3,6}

The improper ferroelectricity observed in the LTI phase is induced as a secondary order by the helical spin density wave via the spin-lattice coupling. Various models based on symmetry properties of the crystal and the magnetic order have been discussed.^{2,5} A ferroelectric (FE) polarization can arise from a third order coupling of two non-collinear components of a magnetic order parameter and the polarization.^{2,7} A helical spin density wave as observed in $Ni_3V_2O_8$ in the LTI phase fulfills the condition for this coupling between the polarization and the magnetic order parameters and it breaks the inversion symmetry of the magnetic structure. A strong spin-lattice interaction couples the lattice to the magnetic order and results in the local displacements with a macroscopic polarization. A microscopic model describing the magnetoelectric coupling in $Ni_3V_2O_8$ was recently developed by Harris et al.⁴ showing that very small atomic displacements can give rise to the observed FE distortions. Therefore, tuning the lattice displacements by controlled introduction of lattice strain will provide a crucial test to the model proposed. This can be achieved, for example, by the application of external pressure.⁸

The way pressure affects the magnetic and FE orders is different from the action of an external magnetic field. The field couples directly to the magnetic moments and affects the magnetic order in aligning the moments with the field. This can stabilize or suppress magnetic phases depending on the field orientation and the specifics of the magnetic order as observed in recent experiments.² The application of external pressure, however, results in a change of the magnetic exchange coupling constants by compressing the lattice, decreasing the interatomic distances, and changing the bond angles between different ions. This in turn will affect the magnetically ordered phases as well as the FE displacements. A dramatic effect of hydrostatic pressure on the ferroelectricity was recently revealed in multiferroic RMn_2O_5 manganites.⁹ We have therefore investigated the effect of hydrostatic pressure on the LTI phase of $Ni_3V_2O_8$ by measuring the FE polarization under high-pressure conditions. The results

are correlated with strong lattice anomalies observed at the LTI \Rightarrow C phase boundary in thermal expansion measurements.

Single crystals of $Ni_3V_2O_8$ (7 mm diameter and 50 mm long) have been grown using the floating zone furnace. For measuring the thermal expansivities along all three crystallographic orientations samples of typical edge length of 2 to 3 mm were cut from the single crystal and mounted in a high-resolution capacitance dilatometer.¹⁰ The FE polarization was measured by employing the pyroelectric current method. The samples were placed in a beryllium-copper clamp cell that allowed for generation of hydrostatic pressures up to 2 GPa.¹¹ The pressure was measured in situ at low temperatures by monitoring the pressure shift of the superconducting transition temperature of high purity lead.¹² The pyroelectric current signal was measured between 2 K and 10 K for a plate-like sample oriented along the b -axis (the axis of the FE polarization) upon cooling and heating with a small poling voltage applied. The FE polarization was determined by integrating the pyroelectric current. The dielectric constant of the same sample was measured using the HP4285A LCZ meter at a frequency of 100 kHz.

At ambient pressure the FE polarization P arises at the phase transition from the HTI phase (sinusoidal spin density wave) to the LTI phase (helical spin modulation) at $T_{C1}=6.5$ K and it drops to zero at the transition into the commensurate magnetic phase ($T_{C2}=3.9$ K). The measured $P(T)$ as shown in the right inset to Fig. 1 is comparable with previous reports.² The dielectric constant ϵ shown in Fig. 1 exhibits a sharp peak at T_{C1} with a small temperature hysteresis (< 0.03 K) and a small but distinct step at the first order phase transition at T_{C2} (left inset of Fig. 1). The transition from the paramagnetic (PM) phase into the HTI phase is also detected in $\epsilon(T)$ in form of a sudden change of slope at $T_N=9.8$ K. Under hydrostatic pressure the peak of ϵ shown in Fig. 2b slightly shifts to lower temperatures, however, the overall shift at 2 GPa is very small, $\Delta T=-0.35$ K. It is remarkable that the peak width increases dramatically above 1.6 GPa. The LTI to HTI phase boundary is well defined by the peak of $\epsilon(T)$. The stability of the ferroelectric LTI phase towards low temperature, however, is difficult to extract from the pressure dependence of the small step-like feature of $\epsilon(T)$ at T_{C2} shown in the inset of Fig. 1. At low pressure T_{C2} increases but at higher pressure the ϵ -step moves into the tail of the large $\epsilon(T)$ -peak and cannot be resolved any further.

Measurements of the FE polarization is the definitive signature of the existence of ferroelectricity and thus provide an unambiguous way to determine the stability range of the FE LTI phase. Fig. 2a shows the FE polarization P at different pressures. The low-temperature drop of P at T_{C2} shifts to higher temperature in accordance with the dielectric constant measurements. At the same time the magnitude of P is dramatically reduced and the spontaneous polarization no longer exists at pressures above 1.64 GPa. At this critical pressure the FE

state is completely suppressed. The onset of ferroelectricity indicated by the rise of the polarization at T_{C1} is consistent with the pressure dependence of the sharp peak of the dielectric constant (Fig. 2b). The peak height of ϵ decreases quickly in analogy with the suppression of the ferroelectric polarization. The pressure-temperature phase diagram for $Ni_3V_2O_8$ shown in Fig. 3 is constructed from the high pressure measurements of both the dielectric constant and the ferroelectric polarization. The phase boundary between the PM and HTI phases was determined from the $\epsilon(T)$ anomaly at T_N (shown in Fig. 1, left inset). T_N slightly increases under pressure whereas T_{C1} decreases. T_{C2} increases with pressure and merges with T_{C1} at a tricritical point at 1.64 GPa and 6.2 K. The ferroelectric LTI phase ends at the tricritical point and above the critical pressure the transition from the incommensurate HTI phase proceeds directly into the commensurate C phase.

The $Ni_3V_2O_8$ compound displays a layered structure and thus is expected to experience an anisotropic strain under a hydrostatic pressure. For a detailed analysis of the pressure effect on the compound, data of compressibility along different crystal axes is required. While compressibility data for $Ni_3V_2O_8$ are not available, measurements of the anisotropy of the thermal expansion and the lattice anomalies at the phase transitions can be utilized to characterize the anisotropic properties of the structure. The thermal expansivities along the principal crystallographic orientations have been measured and the data are displayed in Fig. 4. Whereas small anomalies of the lattice parameters are barely detected at T_N and T_{C1} , the transition from the LTI phase into the C phase at T_{C2} exhibits the largest anomalies in form of sizable abrupt changes of a , b , and c . The anisotropy of these anomalies (a , b expand but c contracts upon cooling through T_{C2}) shows the strongly anisotropic character of the spin-lattice coupling at this transition. Note that the change of the volume V is relatively small though the uniaxial strain along the crystallographic orientations is large. The relative changes of a , b , c , and V upon cooling through T_{C2} as estimated from the dilatometric measurements are $\Delta a/a = 1.65 \times 10^{-5}$, $\Delta b/b = 3.97 \times 10^{-5}$, $\Delta c/c = -8.24 \times 10^{-5}$, and $\Delta V/V = -2.62 \times 10^{-5}$, respectively. The volume of the low-temperature C-phase is smaller than the volume of the LTI-phase which could explain the increase of T_{C2} since pressure will stabilize the smaller volume phase. However, the effects of pressure on the microscopic magnetic exchange constants in the anisotropic structure of $Ni_3V_2O_8$ should be essential as well.

A comprehensive investigation of the magnetic orders by Kenzelmann et al.³ indicates that nearest (NN) and next-nearest (NNN) neighbor superexchange interactions (parameters J_1 and J_2 , respectively), as well as the single ion anisotropy (SA) (parameter K) of the nickel ions at the spine sites of the Kagomé lattice have to be considered as a minimum to understand the sequence of phase transitions from PM \Rightarrow HTI \Rightarrow LTI \Rightarrow C upon

decreasing temperature. A qualitative phase diagram could be constructed by evaluating a one dimensional model in mean field approximation including the effects of NN, NNN, and SA. For a ratio of $J_1/J_2=2.56$, the solution of the model calculation reproduces the IC magnetic orders with the experimentally observed wave vector of $\vec{q}=(0.27,0,0)$. The simplified model does describe the observed sequence of phase transitions if the remaining free parameter K/J_1 is chosen appropriately as $K/J_1=0.6$.³ It is interesting that the model phase diagram, T/J_1 versus K/J_1 , exhibits very similar features as our pressure-temperature phase diagram of Fig. 3. With increasing ratio K/J_1 the Néel transition temperature T_N as well as T_{C2} increase while T_{C1} decreases until it merges with T_{C2} resulting in a tricritical point. According to our high-pressure phase diagram, the external pressure affects all three critical temperatures in exactly the same way as K/J_1 does in the model phase diagram. It therefore appears conceivable that pressure can be considered to increase the model parameter K/J_1 .

The suppression of ferroelectricity by pressure in $Ni_3V_2O_8$ is in contrast to the observation that pressure increases the FE polarization at low temperatures in $HoMn_2O_5$, another multiferroic compound with ferroelectricity induced by frustrated magnetic orders.^{9,13} The major difference between the FE phases in $Ni_3V_2O_8$ and $HoMn_2O_5$ is the commensurability of the magnetic phase associated with the ferroelectricity. The magnetic order in the FE phase in $Ni_3V_2O_8$ is incommensurate whereas it is commensurate in the case of $HoMn_2O_5$. It appears that external pressure always favors the commensurate magnetic orders which can explain the opposite pressure effects in the two multiferroic compounds. In the case of $Ni_3V_2O_8$ the pressure effect can be related to the single ion anisotropy (i.e. the parameter K/J_1) in reference to the simple model discussed before.³ In $HoMn_2O_5$ as well as in other rare earth RMn_2O_5 , however, the role of the magnetic anisotropy in relation to the different magnetic exchange couplings among the Mn^{3+} -, Mn^{4+} -, and R^{3+} -moments is not yet clear.¹⁴

Although the comparison of the model phase diagram³ and the pressure-temperature diagram of this work shows striking similarities, a more detailed experimental as well as theoretical investigation is needed to clarify the effect of pressure on the microscopic exchange coupling and anisotropy constants. A more sophisticated model should take into account the specifics of the 2D Kagomé staircase structure which is a frustrated system by geometry. The interactions between different planes along the b -axis may also play an essential role in stabilizing long-range magnetic and FE orders. Some details have been discussed extensively by Kenzelmann et al.³ and it was found that, besides the NN, NNN, and SA interactions discussed above, much weaker Dzyaloshinskii-Moriya as well as pseudo-dipolar interactions contribute to the complex magnetic orders of the Ni-spine spins and their coupling to the Ni moments at cross-tie positions. An important step towards a microscopic the-

ory of the magnetoelectric effect in $Ni_3V_2O_8$ is the recent work of Harris et al.⁴ Based on inelastic neutron scattering experiments and a first-principles calculation of phonon modes, the most relevant phonons that may give rise to the magnetoelectric coupling and the FE distortions have been identified. The lattice distortions at the FE transitions derived from this investigation are so small that they are hardly observed in neutron scattering experiments. It is the extraordinary high resolution of our dilatometric measurements that allows to detect the lattice strain at the magnetic and FE phase transitions in multiferroic materials.¹³ However, in $Ni_3V_2O_8$, a sizable strain is only seen at the low- T lock-in transition into the commensurate phase, as shown in Fig. 4. At the onset of ferroelectricity at T_{C1} an anomaly of the lattice parameters is barely detectable. It is the symmetry of the magnetic structure and of the associated small non-centrosymmetric displacement of the ions that is essential at this transition resulting in a net FE polarization below T_{C1} . The expansion data prove the strong anisotropy of the structure and the magnetically ordered phases. Any forthcoming theory has to account for the anisotropic character of the system. Experimentally, the anisotropy could be controlled by applying uniaxial pressure along the main crystallographic directions. This would, together with first-principle calculations of the strain dependence of the most important magnetic exchange and anisotropy parameters, facilitate a better understanding of the strain effects on the magnetoelectric coupling in $Ni_3V_2O_8$.

The pressure-temperature phase diagram of Fig. 3 implies that in a narrow temperature range pressure will change the commensurability of the magnetic order as well as the detailed spin alignment in crossing the T_{C2} phase boundary. This prediction should be confirmed by the results of neutron scattering experiments conducted under high-pressure conditions. While the wave vector of the magnetic modulation is sensitive to the ratio of the NN and NNN exchange integrals³ high-pressure neutron scattering is the ideal tool to further investigate the pressure effect on the magnetic coupling parameters. It can be expected that even relatively low pressure does change the characteristic wave vector of the magnetic orders in the HTI and LTI phases. Since big single crystals of $Ni_3V_2O_8$ can be grown in a floating zone furnace these experiments are feasible and they may provide the final key to solve the complex problem of magnetic and ferroelectric orders and their mutual interactions in the multiferroic $Ni_3V_2O_8$.

Acknowledgments

This work is supported in part by the T.L.L. Temple Foundation, the J. J. and R. Moores Endowment, and the State of Texas through TCSUH and at LBNL through the US DOE, Contract No. DE-AC03-76SF00098.

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FIG. 1: Temperature dependence of the dielectric constant of $Ni_3V_2O_8$ near the FE transitions. Full circles: cooling, Open circles: heating. Left inset: Step of ϵ at the lock-in transition into the commensurate phase. Right inset: FE polarization.

FIG. 2: (Color online) Temperature dependence of (a) the FE polarization and (b) the dielectric constant at different pressures. Different $\epsilon(T)$ -curves are vertically offset for better clarity.

FIG. 3: Pressure-temperature phase diagram of $Ni_3V_2O_8$.

FIG. 4: (Color online) Lattice strain along a -, b -, and c -axes below 10 K. The reference length L_0 is the lattice parameter at 10 K.









